

# Exact Density-Functionals for Correlated Dynamics on a Quantum Ring

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We explicitly construct the time-dependent Kohn-Sham potential as a functional of the density and the initial state for a quantum ring with two interacting particles in a singlet state. In this case the initial state is completely determined by the initial density, the initial time-derivative of the density and a single integer that characterizes the (angular) momentum of the system. We give an exact expression for the exchange-correlation potential that produces the exact density of a non-interacting reference system with a different initial state. This is used to demonstrate that the Kohn-Sham procedure correctly predicts the density of a reference system without the need of solving the reference system's Schrödinger equation. We further construct the exchange-correlation potential and frequency-dependent exchange-correlation kernel for an analytically solvable system of two electrons on a quantum ring with a squared cosine two-body interaction.

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Time-dependent density-functional theory (TDDFT) [1, 2] allows for an exact description of a many-body system in terms of an effective non-interacting system, known as the Kohn-Sham (KS) system. The effective external potential (known as the KS potential) in the non-interacting system is a functional of the density in such a way that the KS system has exactly the same density as the reference system. The essential component of the KS potential is the exchange-correlation (xc) potential that contains all nontrivial many-body effects. It depends on the initial states of the interacting and the KS system (initial-state dependence) as well as the density at all previous times (memory). Both features of the xc potential are, however, not well understood and consequently virtually all commonly used approximations neglect them, which in important cases (doubly excited states, molecular dissociation, charge transfer etc.) can lead to large errors in the calculated properties [1, 2]. It is therefore highly desirable to have exact analytical functionals available for model systems that can serve as benchmarks and which can provide insight into the way memory and initial state dependence can be incorporated into approximate functionals for real systems. In this work we explicitly construct such exact functionals of the density and the initial state for the case of a quantum ring (QR) with two interacting particles in a singlet state. We further give an analytic expression for the xc potential that produces the exact density of a non-interacting reference system with a different initial state. We use this to demonstrate that the KS procedure correctly predicts the density of a reference system without the need of solving the Schrödinger equation of the corresponding reference system. We further consider the analytically solvable system of two electrons on a QR with a squared cosine two-particle interaction, for which we construct the xc potential and the frequency-dependent xc kernel of linear response TDDFT.

The Runge-Gross theorem [3] and its generalizations [4, 5] tell us that, for systems with general two-body in-

teractions, the wave function is a functional of the one-particle density  $n(\mathbf{r}, t)$  and of the initial state  $|\Psi_0\rangle$ , i.e.  $|\Psi(t)\rangle = |\Psi([\Psi_0, n], t)\rangle$ . This also applies to the external potential that produces this wave function by propagation of the initial state, i.e.  $v(\mathbf{r}, t) = v([\Psi_0, n], \mathbf{r}, t)$ . Thus the knowledge of the density  $n(\mathbf{r}, t)$  is sufficient, in principle, to calculate all observables of the quantum system. A numerically efficient way to calculate the density is the KS construction, where one uses an auxiliary non-interacting quantum system (the KS system) that produces the same density as the corresponding reference system of interest. The existence of such a KS system in the time-dependent case has been shown in [6] and more general proofs have since been put forward [4, 5]. Since the non-interacting system with initial state  $|\Phi_0\rangle$  also obeys the Runge-Gross theorem, there is a unique potential  $v_s(\mathbf{r}, t) = v_s([\Phi_0, n], \mathbf{r}, t)$  for this system that produces the density  $n$ . We can now define the xc potential by the expression

$$v_s[\Phi_0, n] = v[\Psi_0, n] + v_H[n] + v_{xc}[\Psi_0, \Phi_0, n]. \quad (1)$$

Here the Hartree potential is defined as

$$v_H([n], \mathbf{r}, t) = \int d\mathbf{r}' n(\mathbf{r}', t) w(\mathbf{r}, \mathbf{r}'),$$

where  $w(\mathbf{r}, \mathbf{r}')$  is the two-particle interaction. We further define the KS potential by

$$v_{KS}[\Psi_0, \Phi_0, n] = v_{ext} + v_H[n] + v_{xc}[\Psi_0, \Phi_0, n] \quad (2)$$

where  $v_{ext}$  is the external potential in a reference system that, in general, is taken to be interacting. Suppose we use  $v_{KS}$  as the potential in a non-interacting system with initial state  $|\Phi_0\rangle$  and we solve the resulting nonlinear Schrödinger equation (i.e. the KS equations) self-consistently for the density. Then for the density  $n$  that we obtain we must have, by definition of  $v_s$ , that  $v_{KS}[\Psi_0, \Phi_0, n] = v_s[\Phi_0, n]$ . This then implies, by Eqs.(1) and (2), that  $v[\Psi_0, n] = v_{ext}$ , and therefore the density

that we obtain is identical to the density obtained by solving the Schrödinger equation of the interacting system with initial state  $|\Psi_0\rangle$  and external potential  $v_{\text{ext}}$ .

We will now explicitly construct the functional  $v_s[\Phi_0, n]$  and the functional  $v_{\text{xc}}[\Psi_0, \Phi_0, n]$  for the case that the reference system is non-interacting. This will be done for a one-dimensional two-electron system with periodic boundary conditions, also known as a QR. We start by making the Ansatz

$$\Phi(x, y, t) = \varphi(x, t)\varphi(y, t) \quad (3)$$

for the spatial part of the singlet state KS wave function. The full space-spin dependence is obtained by multiplying by the usual anti-symmetric singlet spin-function. We start by constructing  $\varphi$  as a functional of the density. This orbital is determined by the one-dimensional Schrödinger equation

$$i\partial_t\varphi(x, t) = \left(-\frac{1}{2}\partial_x^2 + v_s(x, t)\right)\varphi(x, t), \quad (4)$$

with periodic boundary conditions on the interval  $[0, L]$  and starting from the initial state  $\varphi_0(x) = \varphi(x, t_0)$ . We then rewrite the orbital in terms of real-valued functions  $|\varphi|$  and  $S$  as [1, 7, 8]

$$\varphi(x, t) = |\varphi(x, t)| \exp(iS(x, t)).$$

The periodic boundary conditions on the orbital then correspond to periodic boundary conditions on  $|\varphi|$  and for the function  $S$  we find

$$S(L, t) = S(0, t) + 2\pi m \quad (5)$$

$$\partial_x S(L, t) = \partial_x S(0, t), \quad (6)$$

for some integer  $m$ . We see that the initial orbital  $\varphi_0(x) = |\varphi_0(x)| \exp(iS_0(x))$  determines the choice of  $m$  since  $S_0(x) = S(x, t_0)$  must obey condition (5). The density and current of the KS system are given by

$$n(x, t) = 2|\varphi(x, t)|^2 \quad (7)$$

$$j(x, t) = n(x, t)\partial_x S(x, t). \quad (8)$$

which are connected via the continuity equation

$$-\partial_x j(x, t) = -\partial_x [n(x, t)\partial_x S(x, t)] = \partial_t n(x, t), \quad (9)$$

and which expresses the local conservation of particles. This is a Sturm-Liouville equation [5] parametrically depending on the time  $t$  and thus the density determines the phase function  $S(x, t)$  for a given set of boundary conditions (5) and (6). More precisely  $S$  is determined uniquely up to a purely time-dependent constant since the constant function is eigenfunction of the Sturm-Liouville operator in (9) with eigenvalue zero and also satisfies the boundary conditions (5) and (6). Physically this freedom amounts to gauge freedom in the potential. Following similar derivations as in [5] we then find that

$$\begin{aligned} S([m, n], x, t) &= \int_0^L dy K_t(x, y)\partial_t n(y, t) \quad (10) \\ &+ \frac{2\pi m}{\int_0^L \frac{dy}{n(y, t)}} \int_0^x \frac{dz}{n(z, t)}, \end{aligned}$$

where we defined

$$\begin{aligned} K_t([n], x, y) &= \frac{1}{2}[\theta(y - x) - \theta(x - y)] \int_y^x \frac{dz}{n(z, t)} \\ &- \frac{\eta(x, t)\eta(y, t)}{\int_0^L \frac{dy}{n(y, t)}}, \end{aligned}$$

with  $\theta$  the Heaviside function and

$$\eta(xt) = \frac{1}{2} \left( \int_0^x \frac{dy}{n(y, t)} + \int_L^x \frac{dy}{n(y, t)} \right).$$

All these functions are defined within the interval  $[0, L]$  and can be extended periodically outside of it. At  $t = t_0$  this equation determines  $S_0(x)$  in terms of  $n(x, t_0)$ ,  $\partial_t n(x, t_0)$  and  $m$  and therefore for a given choice of  $m$  the density completely determines the initial state  $\varphi_0(x)$ . Therefore, if we restrict ourselves to the product Ansatz (3), there is for a given time-dependent density only a countably infinite number of initial states possible.

We can deduce from Eqs. (8) and (10) that the different values of  $m$  correspond to different total momenta  $P(t) = \int_0^L dx j(x, t)$  (or angular momenta if we interpret  $x$  as an angular variable). Thus, the initial states which all have the same initial density and time-derivative of the density but different boundary conditions on the phase, describe differently rotating systems.

The external potential  $v_s$  can readily be expressed in terms of the orbital by inverting the Schrödinger Eq. (4) and we find [1, 7, 8]

$$\begin{aligned} v_s([\varphi], x, t) &= \frac{i\partial_t\varphi(x, t) + \frac{1}{2}\partial_x^2\varphi(x, t)}{\varphi(x, t)} \quad (11) \\ &= \frac{1}{2} \frac{\partial_x^2|\varphi(x, t)|}{|\varphi(x, t)|} - \partial_t S(x, t) - \frac{1}{2} (\partial_x S(x, t))^2 \\ &+ i \left\{ \frac{\partial_t|\varphi(x, t)|}{|\varphi(x, t)|} + \frac{\partial_x|\varphi(x, t)|}{|\varphi(x, t)|} \partial_x S(x, t) + \frac{1}{2} \partial_x^2 S(x, t) \right\}. \end{aligned}$$

The last term on the right hand side vanishes as a consequence of the continuity Eq.(9) and we thus find using  $|\varphi| = \sqrt{n/2}$  that

$$\begin{aligned} v_s([m, n], x, t) &= \frac{1}{2} \frac{\partial_x^2 \sqrt{n(x, t)}}{\sqrt{n(x, t)}} - \partial_t S([m, n], x, t) \\ &- \frac{1}{2} (\partial_x S([m, n], x, t))^2, \quad (12) \end{aligned}$$

which gives  $v_s$  as a functional of  $n$  and the initial state (characterized by  $m$ ). The potential  $v_s[m, n]$  exists whenever we have a unique  $S[m, n]$ , i.e. for  $n > 0$  and the integrability conditions  $\int_0^L dx |1/n(x, t)| < \infty$  and  $\int_0^L dx |\partial_t n(x, t)| < \infty$  are fulfilled [5]. Thus we have analytically defined a density-potential mapping which is also explicitly initial-state dependent. We stress that the periodic boundary conditions on the wave function were essential in deriving Eq.(12). This excludes, for instance,

the example of a homogeneous electric field on a ring of constant density given in reference [9] [15].

Let us now consider the xc potential. The general definition of this potential is according to Eq.(1)

$$v_{\text{xc}}[\Psi_0, \Phi_0, n] = v_s[\Phi_0, n] - v_{\text{H}}[n] - v[\Psi_0, n].$$

The construction of this functional therefore requires the knowledge of the functional  $v[\Psi_0, n]$ . This functional is not explicitly known. However, if the reference system is non-interacting then  $v[\Psi_0, n] = v_s[\Psi_0, n]$  and since in that case  $v_{\text{H}}[n] = 0$  we find that

$$v_{\text{xc}}[\Psi_0, \Phi_0, n] = v_s[\Phi_0, n] - v_s[\Psi_0, n] \quad (13)$$

and hence the KS potential of Eq. (2) is given by

$$v_{\text{KS}}[\Psi_0, \Phi_0, n] = v_{\text{ext}} + v_s[\Phi_0, n] - v_s[\Psi_0, n]. \quad (14)$$

Since for the case of our QR we know the functional  $v_s[\Phi_0, n]$  for the case of a product Ansatz initial state, we can apply expressions (13) and (14). The xc potential is then given by

$$\begin{aligned} v_{\text{xc}}([m, m', n], x, t) &= v_s([m', n], x, t) - v_s([m, n], x, t) \\ &= 2\pi(m - m') \partial_t \left( \frac{\int_0^x \frac{dz}{n(z, t)}}{\int_0^L \frac{dz}{n(z, t)}} \right) + \frac{2\pi^2(m^2 - m'^2)}{\left( n(x, t) \int_0^L \frac{dz}{n(z, t)} \right)^2} \\ &\quad + \frac{2\pi(m - m') \partial_x S([0, n], x, t)}{\int_0^L \frac{dz}{n(z, t)}}. \end{aligned} \quad (15)$$

where  $\partial_x S([0, n], x, t)$  is defined only in terms of  $n$  and  $\partial_t n$  and corresponds to the spatial derivative of the first term on the right hand side of Eq. (10). For the ring system the integer  $m$  plays the role of the initial state  $\Psi_0$  whereas  $m'$  plays the role of the state  $\Phi_0$ . The corresponding KS equations are thus

$$\begin{aligned} i\partial_t \varphi(x, t) &= \left( -\frac{1}{2}\partial_x^2 + v_{\text{ext}}(x, t) \right. \\ &\quad \left. + v_{\text{xc}}([m, m', n], x, t) \right) \varphi(x, t), \end{aligned} \quad (16)$$

$$n(x, t) = 2|\varphi(x, t)|^2, \quad (17)$$

with  $\varphi(x, t_0) = \varphi_0^{m'}(x)$ . This equation now determines the density  $n(x, t)$  of the reference system when we prescribe  $v_{\text{ext}}$ . We note that the xc potential is given only in terms of  $n$  and  $\partial_t n$ . In contrast, the functional  $v_s([m, n], x, t)$  of Eq. (12) that reproduces a *prescribed* density via propagation of the KS equation also contains a second-order time-derivative of the density (in the term  $\partial_t S$  as can be seen with the help of Eq. (10)). We therefore can explicitly see that the second order time-derivative of the density vanishes if we connect the two systems. This is an important fact which sometimes is overlooked in the literature and can lead to misunderstandings about the KS approach [1, 10, 11]. Thus the KS equations (16) and (17) have to be solved self-consistently. The initial state of the reference system

tells what the initial density and initial time-derivative of the density is. The initial state of the KS system must then be chosen such that it gives these quantities correctly. Since the KS potential in Eq.(16) only requires the knowledge of the density and its first time derivative, these initial data determine the solution uniquely.

In the case that the reference system is interacting, we do not know  $v_{\text{xc}}[\Psi_0, \Phi_0, n]$  but we can still calculate it as a function of space and time for a specific density when we can solve the interacting system. This we will now do for the case of two electrons interacting via a squared cosine potential on a QR of length  $L$ . We start by the explicit construction of all the eigenstates of this system. The Hamiltonian is given (in atomic units) by

$$\hat{H} = -\frac{1}{2}(\partial_x^2 + \partial_y^2) + \lambda \cos^2\left(\frac{\pi}{L}(x - y)\right), \quad (18)$$

where  $\lambda$  is the strength of the interaction and  $x$  and  $y$  are the spatial coordinates for the particles along the ring. In this example  $v_{\text{ext}}$  is therefore simply the zero potential. Thus for repulsive interactions the particles will preferably be located where the interaction is zero, i.e. on opposite sides of the ring. For a two-electron system the eigenstates can be written as the product of a spatial wave function  $\Psi(x, y)$  and an (anti)-symmetric spin-function. We have a spin-singlet (spin-triplet) configuration if  $\Psi(x, y)$  is (anti)-symmetric with respect to an interchange of  $x$  and  $y$ , i.e.

$$\Psi(x, y) = \pm \Psi(y, x) \quad (19)$$

where + refers to the singlet state and – to the triplet state. We further have the periodic boundary conditions

$$\begin{aligned} \Psi(x + L, y) &= \Psi(x, y) \\ \Psi(x, y + L) &= \Psi(x, y), \end{aligned}$$

with similar conditions on the spatial derivatives. It is convenient to introduce the center-of-mass  $R = (x + y)/2$  as well as the relative coordinate  $r = x - y$ . In terms of these coordinates the Hamiltonian of Eq.(18) attains the form

$$\hat{H} = -\frac{1}{4}\partial_R^2 - \partial_r^2 + \lambda \cos^2\left(\frac{\pi r}{L}\right). \quad (20)$$

The eigenstates  $\Phi(R, r) = \Psi(x, y)$  in the new coordinates then satisfy the equivalent property of (19)

$$\Phi(R, r) = \pm \Phi(R, -r) \quad (21)$$

and the periodic boundary conditions

$$\Phi(R + \frac{L}{2}, r \pm L) = \Phi(R, r) \quad (22)$$

and similarly for the spatial derivatives. With the Ansatz  $\Phi(R, r) = f(R)g(r)$  the Schrödinger equation can be separated. The periodic boundary conditions on  $f$  and  $g$  become

$$g(r + L) = \pm g(r), \quad (23)$$

$$f(R + L/2) = \pm f(R), \quad (24)$$

and similarly for the spatial derivatives, where the signs on the right hand side of these equations must be the same for  $f$  and  $g$  in order to fulfill Eq.(22). The equation for the center-of-mass coordinate  $R$  becomes a free particle Schrödinger equation

$$-\frac{1}{4}\partial_R^2 f(R) = \epsilon f(R)$$

which has the eigenstates (up to normalization)

$$f(R) = \exp\left(\frac{i2\pi k R}{L}\right)$$

where the boundary conditions with  $\pm$  in Eq.(24) correspond to  $k$  being even and odd respectively. The energy eigenvalue is  $\epsilon = (k\pi/L)^2$ . After changing coordinates to  $z = r\pi/L$  the Schrödinger equation in the relative coordinate becomes

$$\partial_z^2 M(z) + [a - 2q \cos(2z)] M(z) = 0, \quad (25)$$

where we defined  $M(z) = g(Lz/\pi)$ . We further defined

$$\begin{aligned} a &= \frac{L^2}{\pi^2} \left( E - \epsilon - \frac{\lambda}{2} \right), \\ q &= \frac{\lambda L^2}{4\pi^2}, \end{aligned}$$

with  $E$  the eigenenergy of the full Hamiltonian of Eq.(18). The boundary condition (23) then becomes  $M(z + \pi) = \pm M(z)$ . Eq. (25) is the well-known Mathieu equation [13]. The solutions are given by the Mathieu-sine and Mathieu-cosine functions denoted by  $SE(l, q, z)$  and  $CE(l, q, z)$  where  $l$  is a non-negative integer labeling certain discrete values  $a_l$  for the constant  $a$  in Eq.(25). In the limit  $\lambda \rightarrow 0$  (non-interacting case) we simply have  $CE(l, 0, z) = \cos(lz)$  and  $SE(l, 0, z) = \sin(lz)$  and  $a_l = l^2$ . We thus see that the  $\pm$  signs in the boundary conditions (23) correspond to the case that  $l$  is even and odd respectively. From Eq.(21) we see that the singlet and triplet case corresponds to the symmetry  $g(r) = \pm g(-r)$  or equivalently  $M(z) = \pm M(-z)$  for the Mathieu functions. This means that the singlet solution corresponds to the Mathieu-cosine function and the triplet to the Mathieu-sine function. The full solution of the problem is therefore given by

$$\begin{aligned} \Psi_{kl}^+(x, y) &= N_l^+ \exp\left(\frac{i\pi}{L}k(x+y)\right) CE\left(l, q, \frac{\pi}{L}(x-y)\right) \\ \Psi_{kl}^-(x, y) &= N_l^- \exp\left(\frac{i\pi}{L}k(x+y)\right) SE\left(l, q, \frac{\pi}{L}(x-y)\right) \end{aligned}$$

where  $+$  and  $-$  refer to the singlet and triplet cases respectively and  $N_l^\pm$  is a normalization factor. In both cases  $k$  and  $l$  need to be both even or both odd. The associated energy eigenvalues are

$$E_{kl}^\pm = \left(\frac{\pi}{L}\right)^2 \left[ k^2 + a_l^\pm(q) + 2q \right],$$

where  $a_l^\pm(q)$  are the characteristic values for the Mathieu-cosine and Mathieu-sine function respectively [13]. For  $q \neq 0$  the characteristic values obey  $a_0^+(q) < a_1^-(q) < a_1^+(q) < a_2^-(q) < \dots$ , while in the non-interacting case  $a_l^+(0) = a_l^-(0) = l^2$ . We thus nicely see how the two-particle interaction splits the degeneracy of the spin-singlet and spin-triplet states. Independent of the interaction strength the ground state of the QR is the spin-singlet state  $\Psi_{00}^+(x, y)$ . For large values of  $q$  the Mathieu functions become localized around  $z = \pi/2$  (and hence  $r = L/2$ ) corresponding to the strongly correlated limit of well-localized electrons on opposite parts of the ring. The limit  $L \rightarrow \infty$  corresponds to  $q \rightarrow \infty$  and corresponds to a limit where the density goes to zero. This limit corresponds to the famous Wigner crystal [14].

We can now construct the exact xc potential for a specific density  $n$  that corresponds to a solution of the time-dependent Schrödinger equation with Hamiltonian (18). For such a density the xc potential is given by

$$v_{xc} = v_s[m', n] - v_H[n]$$

since in our example  $v_{ext} = 0$ . The xc potential can be further split into an exchange (x) and a correlation (c) part  $v_{xc} = v_x + v_c$  where, for our two-electron system, the x potential is simply given by  $v_x = -(1/2)v_H$  [1]. We choose the density  $n$  to come from a freely propagating superposition of two normalized eigenstates of our QR

$$\begin{aligned} \Psi(x, y, t) &= C_0 \Psi_{00}^+(x, y) \exp(-iE_{00}^+(t - t_0)) \\ &\quad + C_1 \Psi_{11}^+(x, y) \exp(-iE_{11}^+(t - t_0)), \end{aligned}$$

which is a solution to the time-dependent Schrödinger equation. This wave function is properly normalized whenever  $C_0^2 + C_1^2 = 1$ . Note that both eigenstates have a constant density. If the constant  $C_0$  is almost 1 (or 0), the density of the system only deviates slightly from being homogeneous. If we look at a small QR, e.g.  $L = 1$  and different interaction strengths  $\lambda$ , we find that even for small deviations from homogeneity the c potential is at least of the same order of magnitude as the x potential. In this case, increasing the density variations by changing  $C_0$  make the correlation potential  $v_c$  the dominant contribution to  $v_{xc}$ . A notable exception is an initial KS state that has approximately the right initial angular momentum (in the case of  $\lambda = 100$  and  $L = 1$  this is the state  $m' = 1$  as can be seen in Fig. (1)).

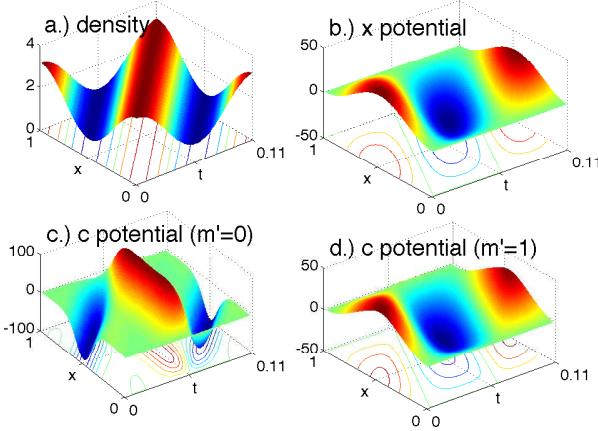


FIG. 1: (color online). The density, x potential and c potentials for  $C_0^2 = 0.5$  and  $m' = 0$  as well as  $m' = 1$  ( $\lambda = 100$ ,  $L = 1$ ). Note the change of scale between  $m' = 0$  and  $m' = 1$ .

Here the c potential plus the x potential mainly needs to cancel the Hartree potential. The KS orbital would travel around the ring in approximately the right manner without any external perturbations. Besides the initial-state dependence one also clearly sees the non-locality of the c potential in time and space, as it has in general no obvious simple relation to the local density (see the c potential for  $m' = 0$  in Fig. (1)). If we go to larger QRs, e.g.  $L = 2\pi$ , the x potential becomes the dominant contribution to the xc potential. This seems counterintuitive since for this case the value of  $q$  is larger, corresponding to a more correlated state. It should, however, be remembered that the relation between the density profile (and hence the shape of  $v_s$ ) and the electronic correlations is rather indirect. For example, the ground state density and KS potential of the QR are spatially constant, independent of the interaction strength. To get more insight into the influence of interactions, it is therefore more useful to study a two-point function. We therefore now will construct the xc kernel, which is defined to be the first functional derivative of  $v_{xc}$  with respect to the density  $n$ , evaluated at the ground state density.

The xc kernel is the central object of interest in linear-response TDDFT from which one can determine the perturbative dynamics of the quantum system and its excitation energies. We start by calculating how the ground state spin-density reacts to small external perturbations, i.e.

$$\delta n(x\sigma, \omega) = \sum_{\sigma'} \int dx' \chi(x\sigma, x'\sigma', \omega) \delta v(x'\sigma', \omega) \quad (26)$$

(see e.g. in Refs. [1, 2]), where

$$\chi(x\sigma, x'\sigma', \omega) = \sum_{kl, p=\pm} \left[ \frac{\langle \Psi_0 | \hat{n}(x\sigma) | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x'\sigma') | \Psi_0 \rangle}{\omega - (E_{kl}^p - E_0) + i\epsilon} - \frac{\langle \Psi_0 | \hat{n}(x'\sigma') | \Psi_{kl}^p \rangle \langle \Psi_{kl}^p | \hat{n}(x\sigma) | \Psi_0 \rangle}{\omega + (E_{kl}^p - E_0) + i\epsilon} \right]$$

with  $\epsilon > 0$  an infinitesimal,  $\hat{n}(x\sigma)$  the usual spin-density operator and  $-\infty \leq k \leq \infty$  and  $0 \leq l \leq \infty$  ( $k$  and  $l$  are always either both even or both odd). Here with  $p = -$  we refer to the triplet state with spin function  $(\delta_{\sigma,\uparrow}\delta_{\sigma',\downarrow} + \delta_{\sigma',\uparrow}\delta_{\sigma,\downarrow})/\sqrt{2}$  since the spin functions orthogonal to this one give a zero contribution in the sum. In a first step we can deduce using the periodicity of the solutions that

$$\begin{aligned} \langle \Psi_0 | \hat{n}(x\sigma) | \Psi_{kl}^+ \rangle &= \exp(i2\pi kx/L) D^+(k, l), \\ \langle \Psi_0 | \hat{n}(x\sigma) | \Psi_{kl}^- \rangle &= \exp(i2\pi kx/L) D^-(k, l) (\delta_{\sigma,\uparrow} - \delta_{\sigma,\downarrow}), \end{aligned}$$

where

$$\begin{aligned} D^+(k, l) &= N_0^+ N_l^+ \int_0^L dr CE\left(0, q, \frac{\pi}{L} r\right) CE\left(l, q, \frac{\pi}{L} r\right) \\ &\quad \times \exp\left(-i\frac{\pi}{L} kr\right), \\ D^-(k, l) &= N_0^+ N_l^- \int_0^L dr CE\left(0, q, \frac{\pi}{L} r\right) SE\left(l, q, \frac{\pi}{L} r\right) \\ &\quad \times \exp\left(-i\frac{\pi}{L} kr\right). \end{aligned}$$

We note that the Mathieu cosine and sine are real and thus we have  $D^\pm(k, l)^* = D^\pm(-k, l)$ . After some manipulations of the general expression for the linear-response kernel we end up with

$$\begin{aligned} \chi(x\sigma, x'\sigma', \omega) &= \sum_k \{ \mu_k^+(\omega) \delta_{\sigma\sigma'} \\ &\quad + \mu_k^-(\omega) [1 - \delta_{\sigma\sigma'}] \} \zeta_k(x) \zeta_k(x')^*, \end{aligned} \quad (27)$$

where

$$\begin{aligned} \zeta_k(x) &= \frac{\exp(i2\pi kx)}{\sqrt{L}}, \\ \mu_k^\pm(\omega) &= \nu_k^+(\omega) \pm \nu_k^-(\omega), \\ \nu_k^\pm(\lambda, \omega) &= \sum_l \frac{2L(E_{kl}^\pm - E_0)|D^\pm(k, l)|^2}{(\omega + i\epsilon)^2 - (E_{kl}^\pm - E_0)^2}, \end{aligned}$$

where the sum runs over all even values of  $l$  if  $k$  is even and over all odd values if  $k$  is odd. In the non-interacting case we find due to  $|D^\pm(k, l)|^2 \rightarrow \delta_{|k|,l}/(2L^2)$  the simple expression

$$\mu_k^{0,+}(\omega) = \frac{1}{L} \left( \frac{2\pi}{L} \right)^2 \frac{k^2}{(\omega + i\epsilon)^2 - \frac{1}{4} \left( \frac{2\pi}{L} \right)^4 k^4}.$$

and  $\mu_k^{0,-}(\omega) = 0$ . In linear-response (spin) TDDFT the interacting response function  $\chi$  is expressed in terms of the non-interacting one  $\chi_0$ , i.e.

$$\chi = \chi_0 + \chi_0 f_{Hxc} \chi, \quad (28)$$

where the Hxc kernel is defined as

$$f_{Hxc} = \chi_0^{-1} - \chi^{-1},$$

and summation as well as integration over reoccurring spin-space variables is implied. With the inverse kernels of Eq. (27) we find that

$$\begin{aligned} f_{\text{Hxc}}(x\sigma, x'\sigma', \omega) &= \sum_{k \neq 0} \left\{ \left( \frac{1}{\mu_k^{0,+}(\omega)} - \frac{\mu_k^+(\omega)}{4\nu_k^+(\omega)\nu_k^-(\omega)} \right) \delta_{\sigma\sigma'} \right. \\ &\quad \left. + \frac{\mu_k^-(\omega)}{4\nu_k^+(\omega)\nu_k^-(\omega)} [1 - \delta_{\sigma\sigma'}] \right\} \zeta_k(x)\zeta_k(x')^*. \end{aligned}$$

The xc kernel is then trivially found by subtracting the interaction potential, i.e.  $f_{\text{xc}} = f_{\text{Hxc}} - w$ . The restriction to  $k \neq 0$  in the sum is a consequence of the fact that the response functions are only invertible in the space of functions orthogonal to the constant function, since a constant potential variation gives no density change. One can therefore add an arbitrary constant to the xc kernel in Eq.(28) without changing  $\chi$ . We have now fully characterized the behavior of the interacting particles on a QR in terms of the KS system for weak external perturbations. The xc kernel exhibits a strong frequency dependence as it needs to shift the poles of  $\chi_0$  and generate new poles in order to have the correct density response

of the correlated system. Needless to say, this is strongly dependent on the interaction strength  $\lambda$  and size of the QR  $L$ .

In conclusion, we presented the exact form of the KS potential for a spin-singlet KS wave function and the explicit form of the xc kernel of linear-response TDDFT in the case of a one-dimensional quantum ring with two interacting electrons. We have illustrated the capability of the presented results to serve as a new benchmark-system for approximations used in TDDFT and presented an exact KS construction. These results will be valuable in deducing new and more reliable functional approximations in TDDFT.

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- [15] If we take  $|\varphi| = \sqrt{n/2}$  to be constant and  $S(x,t) = 2\pi xj/L - x \int_0^t dt' \mathcal{E}(t') + c(t)$  with  $j$  integer, then Eq.(12) yields  $v_s = x\mathcal{E}(t)$  for appropriately chosen  $c(t)$ . This potential describes a homogeneous electric field. However, we see that this choice of  $S$  violates the condition (5) (which should be valid for all times) unless  $\mathcal{E}(t) = 0$ .